

Novel non-cryogenic H₂ storage and spin crossover-assisted gas release in open-metal sites metal-organic frameworks

Hydrogen is looked upon as the next-generation clean-energy carrier. The search for efficient, operationally convenient and cost-effective materials and methods for storing H₂ reversibly is needed to realize the “Hydrogen Economy” and harness the full potential of H₂ generated from excess and intermittent renewable-energy source. However, developing and manufacturing H₂ storage materials that are both cost-effective and scalable for commercial use is a significant challenge. H₂ storage in porous materials is a promising area of research in this concern. In particular, metal-organic frameworks (MOFs) represent a promising family of nanoporous materials for H₂ storage, but for the moment limited to cryogenic conditions, owing to the weak H-bond host-guest interactions taking place in these materials. Yet, a few years ago, it was demonstrated that **ambient temperature storage** can be achieved by employing well-engineered MOFs that exhibit specific open transition metal sites. The mechanism was based on the exploitation of the so-called Kubas mechanism in MOFs exhibiting exposed specific transition metal centers. Exhibiting strong adsorption is indeed the first key factor for efficient storage, but the challenge is that, whenever adsorption is strong, the gas release is energetically costly. Here, **we propose to provide the proof-of-concept** (both computational and with neutron experiments) **for a new H₂ adsorption and release process**. Specifically, we aim at demonstrating the thermodynamic feasibility of strong Kubas adsorption and concomitant spin crossover mediated H₂ release, in such a way that the MOF-H₂ interaction can be tuned from a strong covalent Kubas-like to a weak dispersion-like interaction.

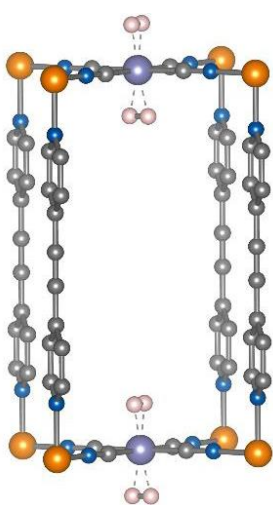


Figure 1: Detail of the structure of $Fe(bpac)M'(CN)_4$ with H₂ molecules adsorbed at the apical sites of the 4-fold coordinated metal M.

We will focus in **Hofmann-type clathrates** (see Figure 1 for an example) exhibiting promising features for an efficient H₂ capture and release, as predicted in our recent work (previous PhD project funded by the ILL). The PhD candidate will combine calculations (SIMaP) and experiments (ILL). The mechanism of H₂ binding will be studied by neutron diffraction and by inelastic neutron scattering. Density-functional theory will be employed to study the electronic structure of these metal-organic frameworks and to assist the interpretation of neutron data. The PhD student working on this project will contribute in an original manner to a broader research project on spin crossover assisted H₂ release. As such, the first experimental verification of the idea will be performed in conjunction by ILL and SIMaP, with synthesis performed at IMDEA (Spain)

Skills. We seek for a highly motivated student with background in physical chemistry or physics with some experience in either large facilities and neutron diffraction or ab initio simulations. For further detail, please contact the supervisors.

Supervisors & contact info: Roberta Poloni (roberta.poloni@grenoble-inp.fr), supervisor on the ab initio calculations, Alberto Rodriguez Velamazán (velamazan@ill.fr) supervisor at ILL. Send them an email with your CV, motivation letter, grade transcripts (master and bachelor), and contact information of two referees that will be asked to send a recommendation letter.

Starting date: October/November 2024 at the latest